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- (54) Title of the Invention: An Antifreezing Agent  
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## SPECIFICATION

### 1. Title of the Invention

An Antifreezing Agent

### 2. Claims

- 1) An antifreezing agent comprising  
1st) at least 1 salt, selected from alkali metallic salts, alkali earth metallic salts and ammonium salts of inorganic acids, and  
2nd) methyl glucoside.
- 2) The antifreezing agent according to Claim 1, which is characterized by the fact, that the alkali metallic salt of the inorganic acid contains at least sodium chloride.
- 3) The antifreezing agent according to Claims 1 and 2, which is characterized by the fact, that it contains at least 1 compound, selected from adipic acid, glutamic acid and benzoic acid.

### 3. Detailed Description of the Invention

#### [Field of Industrial Utilization]

The present invention concerns an antifreezing agent used in road surfaces, etc.

More specifically, it concerns a novel antifreezing agent with improved phytotoxicity with respect to animals and plants, which particularly prevents metallic corrosion.

#### [Prior Art]

In the past, various methods were considered to prevent freezing of road surfaces, and one of these methods, commonly used, was to disperse antifreezing agents, whose main ingredient was a salt of an inorganic acid, such as calcium chloride and sodium chloride. The drawbacks of such conventional antifreezing agents include, however, their corrosive effect on the metallic parts of cars, etc., the blight they cause in plants and their phytotoxicity in humans and animals. Therefore, in order to reduce metal corrosion, phosphate-based or amino-based antirust agents had to be mixed into the conventional products.

In addition, various methods were proposed in order to improve the above-mentioned antifreezing agents. For example, in Japanese Patent Publication 48-68481, reduction of the corrosive effect on metallic parts of cars, etc., and of the phytotoxicity in animals and plants, by using an antifreezing agent containing urea and an ammonium salt of an inorganic acid, was disclosed. In addition, in Japanese Patent Publication 62-89785, a thawing and antifreezing agent with a specific composition, comprising a salt selected

from magnesium chloride and magnesium sulfate as the main ingredient, which practically contains no common salt, and whose isothermal line passes in the area of 3°C or higher, was disclosed, and reportedly, its thawing and antifreezing effect was high, while it had almost no phytotoxicity in plants.

#### [Problems Which the Present Invention Attempts to Solve]

Nevertheless, the improvements proposed, with respect to the corrosive effect on the metallic parts of cars etc., and to the phytotoxicity in animals and plants, of these conventional antifreezing agents, were not satisfactory, and a antifreezing agent free of these undesirable effects has been sought.

The objective of the present invention is to solve these problems pertaining to the prior art, and to propose an antifreezing agent with a superior antifreezing effect yet with no corrosive effect on the metallic parts of cars, etc., on roads, and no phytotoxicity in animals and plants.

#### [Means Used to Solve the Above-Mentioned Problems]

As a result of a painstaking research, aimed at solving the above-mentioned problems, pertaining to antifreezing agents, the inventors arrived at the present invention after discovering that an antifreezing agent, with a superior antifreezing effect yet with no metal corrosiveness or phytotoxicity in animals and plants, can be obtained by using a novel specific composition.

In other words, the present invention concerns an antifreezing agent comprising (A) at least 1 salt, selected from alkali metallic salts, alkali earth metallic salts and ammonium salts of inorganic acids, and (B) methyl glucoside.

The antifreezing agent pertaining to the present invention will now be described in concrete terms.

Specific examples of the alkali metallic salts of inorganic acids, used as an ingredient of the antifreezing agent pertaining to the present invention, include sodium chloride (rock salt), potassium chloride, sodium sulfate, sodium phosphate, and the like. Examples of the alkali earth metallic salts include calcium chloride, magnesium chloride, and the like. And examples of the ammonium salts of an inorganic acid include ammonium sulfate, ammonium phosphate, and the like.

In the antifreezing agent pertaining to the present invention, 1 salt alone or a combination of 2 or more salts, selected from the above-mentioned alkali metallic salts, alkali earth metallic salts and ammonium salts of inorganic acids, can be used.

However, if a salt of the above-mentioned inorganic acids is used as the antifreezing agent, problems of corrosion of the metallic parts of cars and of phytotoxicity in animals

and plant inevitably rise. It is also known that such problems were particularly severe when antifreezing agents containing calcium chloride were used.

In order to solve such problems in the antifreezing agent pertaining to the present invention, it is characterized by the fact that methyl glucoside is used as its main ingredient. Because methyl glucoside is produced using corn starch of maize as the raw material, it has no corrosive effect on metals and no phytotoxicity in animals and plants, and its safety is high. While especially the calcium chloride contained in the conventional antifreezing agents, is known to have a strong corrosive effect on metals and phytotoxicity in animals and plants, because in the antifreezing agent pertaining to the present invention calcium chloride is used together with methyl glucoside, such salt injury can be prevented.

Two optical isomers of methyl glucoside,  $\alpha$  and  $\beta$ , exist, and while normally a mixture of both is used, any content ratio of the two can be used. In addition, the solubility of methyl glucoside in water is such that 100g or more methyl glucoside readily dissolve in 100g water. Consequentially, the antifreezing agent has the necessary properties of solubility and quick curing.

With regard to the antifreezing effect of methyl glucoside, although when methyl glucoside is dissolved in water the freezing temperature decreases to  $-5^{\circ}\text{C}$ , the content of the methyl glucoside in the water, i.e., its aqueous solution concentration, has to be 8% (wt%), at such a concentration, the antifreezing effect obtained is significantly superior in comparison with 8% (wt%) sodium chloride or 6.7% (wt%) calcium chloride.

The ratio of the salt of the inorganic acid and the methyl glucoside, used in the antifreezing agent pertaining to the present invention, should be within the range of 20~25:75~78. If the content of the salt of the inorganic acid exceeds this range, the metal corrosiveness and phytotoxicity in animals and plants of the antifreezing agent increases, while if the content of the methyl glucoside exceeds this range, the metal corrosiveness and phytotoxicity in animals and plants decrease, but the antifreezing effect also somewhat decreases.

In order to prevent the metallic corrosiveness of by-products in the antifreezing agent pertaining to the present invention, it is recommended to add at least one of adipic acid or glutamic acid, and the recommended quantities with respect to the total quantity is between 0.4 and 0.6wt% for adipic acid and between 0.8 and 1.0wt% for glutamic acid. In addition, as a stabilizer for the antifreezing agent pertaining to the present invention, it is recommended to use benzoic acid, at a quantity ranging between 0.2 and 0.4wt% with respect to the total quantity. Other than these, additives which are normally used in antifreezing agents can be mixed into the antifreezing agent, as needed. For example, coal powder, charcoal powder and other heat absorbents, various inorganic or organic coloring agents, and the like, can be used.

The antifreezing agent pertaining to the present invention can be produced by mixing the various ingredients, i.e., the salt of an inorganic acid, methyl glucoside, adipic acid,

glutamic acid, benzoic acid and other additives, using a commonly-known mixing device such as a blender, tumbler or the like. The mixture obtained can be used as it is, as a powder, or the powder mixed can be made into granules, using a pressing machine or the like. Because such a granular antifreezing agent is readily absorbed and the persistency of its antifreezing effect is increased, it has superior applicability. In addition, depending on the purpose of its application, it can be used as an aqueous solution with an adequate concentration.

As described above, due to the fact that the antifreezing agent pertaining to the present invention contains, as its main ingredient, methyl glucoside, manufactured from corn starch as the raw material, in addition to its excellent antifreezing effect, it does not cause metallic corrosion and it has no phytotoxicity in humans, animals or plants, and its safety is significantly superior to that of conventional antifreezing agents. While in conventional antifreezing agents, especially the calcium chloride used had a strong metallic corrosiveness and phytotoxicity in animals and plants, in the antifreezing agent pertaining to the present invention, such salt injury is reduced by the combined use of methyl glucoside, yielding a superior antifreezing agent.

In other words, the antifreezing agent pertaining to the present invention can therefore be safely used as a thawing agent and antifreezing agent in a wide range of places such as roads, factories, houses etc.

#### [Effect of the Invention]

Due to the fact that methyl glucoside is used as a main ingredient in the antifreezing agent pertaining to the present invention, it has an excellent antifreezing effect, and at the same time it has no metallic corrosiveness or phytotoxicity in humans, animals or plants, and it is therefore characterized by superior safety. It has, therefore, many advantages in practical application, such as that it can be used in a wide range of places and is easily stored and transported.

The present invention will now be described by means of practical examples. The present invention is not limited, however, to or by these practical examples.

#### Practical Example 1

25g sodium chloride, 73g methyl glucoside, 0.6g adipic acid, 1.0g glutamic acid and 0.4g benzoic acid were mixed for approximately 15 minutes using Henschel mixer, yielding the mixture pertaining to the present invention. The mixture was subjected to the following tests.

#### Molten ice volume test

250ml tap water was put into a 500ml hollow beaker and left for 24 hours in a refrigerator, at  $-5^{\circ}\text{C}$ , yielding ice. Next, 20g of the above-mentioned mixture, at  $0^{\circ}\text{C}$ , were evenly dispersed on the surface of the ice, and placed in the refrigerator at  $-5^{\circ}\text{C}$ . At

set times after the mixture was dispersed, the beaker was taken out, and the quantities of water produced from the thawed ice were measured. The value shown for each measurement is the average value of 3 tests. The results are shown in Table 1.

#### Corrosiveness test

A 3% aqueous solution of the above-mentioned mixture was prepared, a test piece of [illegible] SS41 was immersed in the aqueous solution and left in a 20°C thermostatic room. After it was immersed for 1 day, the test piece was taken out and left for 1 day at room temperature. This cycle was repeated and after 7 days the change in the weight of the test piece was measured, and the corrosion rate (mdd) was calculated. The results are shown in Table 2.

#### Plant test

A 35% aqueous solution of the above-mentioned mixture was prepared and sprinkled on growing maize, *daikon* [Japanese white reddish] and spinach, using a watering can, 2 times per day, continuously for 4 days, and changes in the condition of the plants were observed. The results are shown in Table 3.

#### Deleterious material test

Using the above-mentioned 35% aqueous solution of the mixture, the content of deleterious material, with respect to the human organs, was measured using the test method of JISK0102. The results are shown in Table 4.

#### Practical Examples 2 through 4

Based on Practical Example 1, calcium chloride (Practical Example 2), a mixture of calcium chloride and magnesium chloride (weight ratio: 50:50) (Practical Example 3) and ammonium sulfate (Practical Example 4) were used in place of sodium chloride, and the same molten ice volume test, corrosiveness test and plant test as in Practical Example 1 were conducted. The results are shown in Tables 1, 2 and 3, respectively.

#### Comparative Example 1

Based on Practical Example 1, only sodium chloride, used in conventional antifreezing agents, was used in place of the mixture of sodium chloride and methyl glucoside, and the same molten ice volume test, corrosiveness test and plant test were conducted as in Practical Example 1. The results are shown in Tables 1, 2 and 3, respectively.

#### Comparative Example 2 through 5

Based on Comparative Example 1, calcium chloride (Practical Example 2), a mixture of calcium chloride and magnesium chloride (weight ratio: 50:50) (Practical Example 3) and ammonium sulfate (Practical Example 4) were used in place of sodium chloride, and the

Comparative Example 2	+	+	X
Comparative Example 3	+	+	X
Comparative Example 4	+	+	X

The evaluation standards were:

- 0: No abnormal growth
- +: Partially abnormal growth
- X: Completely abnormal growth

Table 4 Deleterious material test

Type of deleterious material	Practical Example 1	Practical Example 2
Cadmium and its compounds	0.1mmg	0.001mmg
Cyan compounds	0.1mmg	0
organophosphorous compounds	1mmg	0
Lead and its compounds	1mmg lead	0.01mg lead
Chromium VI compounds	0.5mg chromium VI	0
Mercury and alkali mercury	0	0
Alkali mercury compounds	0	0

Based on the above results, it appears that the antifreezing agent pertaining to the present invention has an excellent antifreezing effect, and at the same time, it is characterized by not having a metal corrosive effect or phytotoxicity in humans or plants, in comparison with conventional products.